Requested Patent: EP0550922A1

Title:

EXTRUDED CATALYST BASED ON SILICA/ALUMINA GEL, AND PROCESS FOR PREPARING IT. ;

Abstracted Patent: EP0550922 ;

Publication Date: 1993-07-14 ;

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Application Number: EP19920203734 19921203 ;

Priority Number(s): IT1991MI03276 19911206 ;

IPC Classification: B01J21/12; B01J37/00; C07C2/10 ;

Equivalents: DE69210002D, DE69210002T, IT1252647, NO301967B, US5342814 ;

ABSTRACT:

The preparation is disclosed of an extruded catalyst based on a silica/alumina gel, which catalyst is particularly active in acid-catalysed reactions, such as the oligomerization of light olefins, e.g., propylene.

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 550 922 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **92203734.6**

(22) Date of filing: **03.12.92**

(51) Int. Cl.5: **B01J 21/12**, B01J 37/00, C07C 2/10

(30) Priority: **06.12.91 IT MI913276**

(43) Date of publication of application: **14.07.93 Bulletin 93/28**

(84) Designated Contracting States: **DE DK FR NL**

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(54) Extruded catalyst based on silica/alumina gel, and process for preparing it.

(57) The preparation is disclosed of an extruded catalyst based on a silica/alumina gel, which catalyst is particularly active in acid-catalysed reactions, such as the oligomerization of light olefins, e.g., propylene.

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The present invention relates to a catalyst in extruded form, based on silica/alumina gel, and to the process for preparing it. The invention also relates to the use of such a catalyst in olefin oligomerization processes.

Some silica/alumina gels, of amorphous character, displaying catalytic activity, are known in the art. So, e.g., European patent application published with publication No. 160,145 discloses a process of alkylation of aromatic hydrocarbons which uses a catalyst consisting of a silica/alumina gel, of amorphous character, with pore diameter tipically comprised within the range of from 50 to 500 Angstrom, and with a ratio of silica to alumina tipically comprised within the range of from 1 : 1 to 10 : 1. M.R.S. Manton and J. Davidtz in Journal of Catalysis, 60, 156-166 (1979) describe a process for the synthesis for amorphous silica/alumina catalysts, having a controlled pore diameter. Tipically, these catalysts display pores with diameter comprised within the range of from 3.7 to 15 nm.

European patent application No. 340,868 discloses a silica/alumina gel, amorphous at X rays, having a molar ratio of SiO_2/Al_2O_3 of from 30 : 1 to 500 : 1, with a specific surface area comprised within the range of from 500 to 1000 m^2/g, a total pore volume of from 0.3 to 0.6 ml/g, and substantially free from pores with larger diameter than 30 Angstrom.

However, the problem exists of rendering industrially useable the silica/alumina gel disclosed in the above said patent application by endowing it with adequate properties of mechanical strength, without endangering the high catalytic performance thereof.

Those skilled in the art are aware of the possible procedures for preparing extruded bodies having high enough mechanical strength values, with their catalytic performace being the same. Thus, for example, the catalyst can be ground, so as to obtain powders consisting of particles with an average size comprised within the range of from 5 to 50 microns, and subsequently blending them with a thickener, for example, stearine, glycerol, methylcellulose.

According to another route of preparation of the extruded catalyst, the catalyst is ground and then is suspended, with vigourous stirring, in an aqueous solution of a soluble aluminum salt. The addition of a base makes it possible aluminum hydroxide to be precipitated, with the catalyst particles getting embedded inside said precipitate particles. A further method consists in mixing silica/alumina gel powders with a second powder selected from metal oxides in the presence of a thickener, for example, stearine, glycerol, methylcellulose.

All of the techniques cited hereinabove should make it possible extrudates to be obtained, which are endowed with such a high mechanical strength as to enable them to be used at an industrial level, with the catalytic properties of silica/alumina gel remaining unchanged.

It has been found now that one of the above said techniques leads to catalysts showing the necessary mechanical strength, but which, surprisingly, are more active in catalysing the usual petrochemical acid-catalysed reactions, such as alkylation, isomerization and oligomerization.

In accordance therewith, according to a first aspect thereof, the present invention relates to a catalyst consisting of:

- an inert binding agent, and
- a catalytically active portion, constituted by a silica/alumina gel, amorphous at X rays, with SiO_2/Al_2O_3 being in a molar ratio comprised within the range of from 30 : 1 to 500 : 1, having a total pore volume comprised within the range of from 0.3 to 0.6 ml/g, and substantially free from pores having a longer average diameter than 30 Angstrom,

characterized in that:

- the inert binding agent is constituted by alumina grades belonging to the class of bohemite or of pseudobohemite.

The aluminas used in the present invention as binding agents in order to extrude the silica/alumina gel have the general formula

AlO-OH.

In the preferred form of practical embodiment of the present invention, bohemite or pseudobohemite have a shorter average diameter than 50 microns, and are present in a ratio to silica/alumina gel comprised within the range of from 0.2 to 2.5 by weight.

The catalyst according to the present invention is suitably prepared by means of a first mechanical mixing of the active phase, i.e., of silica/alumina gel ground until a powder having a shorter average diameter than 50 microns, with the inert binding agent belonging to the class of bohemites or pseudobohemites, or mixtures thereof.

The mixing of the active phase with the inert binding agent is carried out in the presence of a large enough amount of thickener as to produce a paste having the desired viscosity. The mixing in continued until a homogeneous phase is formed. The thickener may be water, an aqueous solution of methylcellulose, stearine, glycerol and so forth. The thickener contains a mineral or organic acid in an amount comprised within the range of from 0.5 to 8 grams of acid per 100 g of inert binding agent. According to another form of practical embodiment, the acid is added to the paste and the resulting mixture is homogenized.

The resulting paste is then extruded and cylindrical bodies of catalyst are obtained, the dimensions of which may be varied as a function of the application requirements.

The extrudate is subsequently submitted to ageing at a temperature of from 10 to 40 °C, and then to drying at 100-120 °C.

The end step consists of the calcination in air at a temperature comprised within the range of from 500 to 600 °C.

The catalyst obtained in that way displays a higher catalytic activity than of the silica/alumina gel used as the starting materials, and furthermore is useable at an industrial level, by having an axial breaking strength comprised within the range of from 20 to 80 kg/cm^2 and a radial breaking strength comprised within the range of from 3 to 8.5 kg/cm.

Important features of the catalyst according to the present invention are the bimodal distribution of porosity, a surface area comprised within the range of from 300 to 600 m^2/g, and a high acidity.

The catalyst according to the present invention can be suitably used in the usual petrochemical acid-catalysed reactions, such as alkylation, isomerization and oligomerization of light olefins, in particular of propylene.

In particular, the catalyst according to the present invention is very effective in the reaction of oligomerization of light olefins, in particular propylene, in order to yield hydrocarbon cuts showing extremely good qualities as gasoline and jet fuel.

The following experimental examples are reported in order to illustrate the present invention in greater detail.

EXAMPLE 1

Catalyst preparation

40 g of Al-Si gel, prepared as disclosed in European patent application No. 340,868 is ground in a ball mill and then is micronized until a powder is obtained with an average distribution of particles comprised within the range of from 10 to 50 microns. To such a powder, 40 g of a commercial pseudobohemite (CATAPAL B - VISTA CHEMICAL COMPANY) is blended by means of a mechanical mixing procedure. Separately, an aqueous solution of methylcellulose (METOCEL FLUKA 64625) at 1% by weight is prepared and is acidified with 0.63 g of glacial CH_3COOH (99.8% by weight).

The acidified aqueous methylcellulose solution (60-70 g) and the powder are now thoroughly mixed, until a homogeneous paste is obtained.

After performing the extrusion, the extrudate is submitted to a 4-hour ageing at room temperature, the aged extrudate is dried at 100 °C for 5 hours, and is calcined at 550 °C for 8 hours in air.

At the end of this operation, the catalyst shows a mechanical strength of 6.4 kg/cm in radial direction and of 42 kg/cm^2 in axial direction, and a specific surface are a of 460 m^2/g.

EXAMPLE 2A

Propylene oligomerization

The extruded catalyst obtained as disclosed in Example 1 was tested in the reaction of propylene oligomerization under the following operating conditions:

- catalyst shape: cylindrical extruded body;
- catalyst dimensions: average diameter approximately 3 mm, average length approximately 5 mm;
- reactor type: fixed bed;
- reactor dimensions: inner diameter = 36 mm, length = 600 mm;
- feed: propylene/propane mixture in the ratio of 35 : 65 by weight;
- reactor temperature: from 100 to 250 °C;
- reactor pressure: from 30 to 50 bars;
- space velocity WHSV: from 0.5 to 2 g of propylene per gram of active phase per hour.

The results are reported in Table 1.

Table 1

WHSV h^{-1}	Pressure bar	Temperature °C	Conversion rate, %
2	30	140	20
1	30	140	30
1	40	140	37
1	50	150	52
1	40	150	46
0.5	40	150	65
0.5	40	160	72

The product obtained from the oligomerization is then distilled, with a fraction useable as gasoline and a fraction useable as jet fuel being obtained.

The gasoline fraction displays the following characteristics:

RON	96,8
MON	82,2
d_{15}	0,7478
C_1-C_4 (% by weight)	1
13-80 °C (% by weight)	3,96
80-175 °C (%by weight)	42,32
175 + (% by weight)	45,72
Olefins (% by weight)	99
Saturated compunds (% by weight)	1
Aromatics (% by weight)	0

The jet fuel fraction displays the following characteristics:

Aromatics, % by volume (ASTM D1319)	1.8
Freezing point, °C (ASTM D2386)	60
Smoke point, mm (ASTM D1322)	38
Gums, mg/100 ml (ASTM D381)	49
Flash point, °C (ASTM D3828)	38
Density at 15°C (ASTM D1298)	0.7718
Distillation (ASTM D86):	
* incipient boiling point (°C):	140
* 10% by volume (°C)	149
* 20% by volume (°C)	157
* 50% by volume (°C)	184
* 90% by volume (°C)	264
* end point (°C):	304

EXAMPLE 2B

Propylene oligomerization

The extruded catalyst obtained as disclosed in Example 1 was tested in the reaction of propylene oligomerization under the following operating conditions:

- catalyst shape: cylindrical extruded body;
- catalyst dimensions: average diameter approximately 3 mm, average length approximately 5 mm;
- reactor type: fixed bed;
- reactor dimensions: inner diameter = 36 mm, length = 600 mm;
- feed: propylene/propane mixture in the ratio of 70 : 30 by weight;
- reactor temperature: from 100 to 250 °C;
- reactor pressure: 50 bars;
- space velocity WHSV: 2 g of propylene per gram of active phase per hour.

The oligomerization productivity rate resulted to be of 900 g of oligomerized product per each gram of active catalyst portion.

COMPARISON EXAMPLE 1

Preparation of a catalytic extrudate by mixing the active phase with a thickener

80 g of Al-Si gel, prepared as disclosed in European patent application No. 340,868, is ground in a ball mill and then is micronized until a powder is obtained which has an average particle distribution comprised within the range of from 10 to 50 microns. Such a powder is slowly added to 40 g of water-alcohol solution of methylcellulose (METOCEL FLUKA 64625) at 1% by weight, with an effective mechanical stirring. The resulting homogeneous paste is allowed to age for approximately 1 hour, then is extruded. The extrudate, having a size comprised within the range of from 3 to 5 mm, is firstly dried at 150 °C for 5 hours and then is calcined at 500 °C for 8-10 hours. At the end of this operation, the catalyst displays a low mechanical strength.

COMPARISON EXAMPLE 2

Preparation of a catalytic extrudate by precipitation of aluminum hydroxide

40 g of Al-Si gel, prepared as disclosed in European patent appplication No. 340,868, is ground in a ball mill and then is micronized until a powder is obtained which has an average particle distribution comprised within the range of from 10 to 50 microns. The powder is added to 905.6 g of an aqueous solution at 11.6% by weight of $Al_2(SO_4)_3$, kept vigorously stirred. NH_4OH at 30% by weight is added, until a pH value of 9 is obtained. The resulting precipitate is washed and filtered repeatedly, until neutral. The resulting solid material, after being dried at 100 °C for 2 hours and calcined overnight at 500 °C, is ground and micronized again until a granulometric distribution comprised within the range of from 10 to 50 microns is obtained. Such a powder is slowly added to 72 g of water-alcohol solution of methylcellulose (METOCEL FLUKA 64625) at 1% by weight, with an effective mechanical stirring. The resulting homogeneous paste is allowed to age for approximately 1 hour, then is extruded. The extrudate, having a size comprised within the range of from 3 to 5 mm, is firstly dried at 150 °C for 5 hours and then is calcined at 500 °C for 8-10 hours. At the end of this operation, the catalyst displays a mechanical strength of 1.4 kg/cm in radial direction and of 14 kg/cm^2 in radial direction, and a specific surface area of 333 m^2/g.

The resulting extrudate is tested as disclosed in Example 1 (Table 2).

Table 2

WHSV h^{-1}	Pressure bar	Temperature °C	Conversion rate, %
2	30	140	3
1	30	140	4
1	40	140	5
1	50	150	8
0.5	40	150	15
0.5	40	160	22

The catalyst is also tested as disclosed in Example 2B, risulting in a productivity rate of 300 g of oligomers per each gram of catalytically active portion.

COMPARISON EXAMPLE 3

Preparation of unbound silica/alumina gel

The catalyst, prepared as disclosed in European patent application No. 340,868 was tested for propylene oligomerization according to as disclosed in Example 2A. The results are reported in Table 3.

Table 3

WHSV h^{-1}	Pressure bar	Temperature °C	Conversion rate, %
2	30	140	3
1	30	140	5
1	40	140	6
1	50	150	10
0.5	40	150	20
0.5	40	160	29

The data of catalytic activity sets forth the better performance of the catalyst according to the present invention as compared to the same catalyst without binding agent, as well as to the catalyst obtained by means of other tecniques.

Claims

1. Catalyst consisting of:
   - an inert binding agent, and
   - a catalytically active portion, constituted by a silica/alumina gel, amorphous at X rays, with SiO_2/Al_2O_3 being in a molar ratio comprised within the range of from 30 : 1 to 500 : 1, having a total pore volume comprised within the range of from 0.3 to 0.6 ml/g, and substantially free from pores having a longer average diameter than 30 Angstrom,

   characterized in that:
   - the inert binding agent is constituted by alumina grades belonging to the class of bohemite or of pseudobohemite.

2. Catalyst according to claim 1, characterized in that bohemite or pseudobohemite have an average diameter shorter than 50 microns, and are present in a ratio to silica/alumina gel comprised within the range of from 0.2 to 2.5 by weight.

3. Process for preparing the catalyst according to claims from 1 to 2, characterized in that the active portion is mixed with the inert phase, in the presence of a thickener containing a mineral or organic acid in an amount comprised within the range of from 0.5 to 8 g of acid per 100 g of inert binding agent, until a homogeneous paste is obtained which is subsequently extruded, yielding cylindrical bodies of catalyst which are eventually submitted to:

- ageing at a temperature comprised within the range of from 10 to 40 °C;
- drying at a temperature comprised within the range of from 100 to 120 °C;
- calcination in air at a temperature comprised within the range of from 500 to 600 °C.

4. Use of the catalyst according to claims from 1 to 2 in acid-catalyzed reaction.

5. Use of the catalyst according to claims from 1 to 2 in the oligomerization of light olefins.

6. Use of the catalyst according to claims from 1 to 2 in propylene oligomerization.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 92 20 3734

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	US-A-5 051 386 (J. W. WARD) * claims 1,9,14; table A * * column 7, line 22 - line 35 *	1,2,4-6	B01J21/12 B01J37/00 C07C2/10
D,Y	EP-A-0 340 868 (ENIRICERCHE) * claims 1,13 *	1,2,4-6	
A	US-A-4 174 301 (M. E. CHOCA)	3	
A	US-A-4 238 361 (H. ALAFANDI)		

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

B01J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	26 APRIL 1993	THION M.A.

CATEGORY OF CITED DOCUMENTS

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